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THE PATENT OFFICE LONDON

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(54) HEAT-RESISTANT ALLOYS

(71) We, NIPPON STEEL CORPORATION, a Japanese Company, of No. 6-3, 2-chome, Ote-machi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to heat-resistant alloys and particularly to such alloys having excellent hot-working characteristics.

Heat-resistant alloys are used in applications such as furnace parts, burner nozzles, annealing boxes and protecting tubes for thermocouples, and in recent years such alloys have been widely used for components of atomic piles. These alloys are usually deformed to produce the required shape at high temperatures (i.e. hot-worked). Since hot-working makes use of the characteristic of the alloys that they soften at high temperatures, hot-working thus has the advantage that products of good dimensional accuracy can easily be obtained when employing only a small working power.

A widely used heat-resistant material which has a suitable hot-working characteristic is an austenite steel containing 7 to 20% of nickel and 14 to 25% of chromium. However, this known heat-resistant alloy steel, and other similar alloys contain Si and W so as to increase the hardness and tensile strength as well as wear resistance at high temperatures, and there are at present very few heat-resistant alloys which have intentionally improved hot-working characteristics.

In recent years, the plants of the chemical industry and other industries have been enlarged, and large constructional heat-resistant components have been demanded therefor. Heat-resistant steel materials used for such large constructional components are subjected to severe production conditions, often starting from a large alloy ingot which is deformed to produce a wide and thin material. The known alloys usually display the defect that they are susceptible to hot-working cracking during the production process, or during the secondary working step for obtaining a predetermined form.

The invention provides a heat-resistant alloy consisting of (by weight) from 0.01 to 0.5% of C, from 0.01 to 2.0% of Si, from 0.01 to 3.0% of Mn, from 22 to 80% of Ni, and from 10 to 40% of Cr as basic constituents; together with one or both of from

0.0005 to 0.20% of B, and from 0.001 to 6.0% of Zr; and one or more of from 0.001 to 0.50% of Ce, from 0.001 to 0.2% of Mg, from 0.001 to 1.0% of Be; the alloy optionally containing from 0.05 to 10% of Y, with the remainder being Fe and unavoidable impurities, the alloy always containing one or both of Y and Ce, and at least some Fe.

It is found that such an alloy has good heat-resistant properties, and displays good hot-working characteristics.

According to another aspect of the invention, a modification of the just-described alloy is provided, which modified alloy additionally comprises (by weight) one or more of from 0.1 to 10.0% of Mo, from 0.1 to 10.0% of W, and from 0.1 to 30% of Co, and, as further constituents, one or more of Ti, Nb, Ta, Al, V, Cu, each, when present, being in the range of from 0.05 to 10%, which further constituents and Y if present together comprise between 0.05 and 10% of the total weight of the alloy.

It will be appreciated that this invention is based on the discovery that when B, Zr, Ce, Mg, Be and optionally Y are selectively added in combination to a high-nickel and high-chromium austenitic steel, the torsion numbers of the alloy so formed can be increased, especially at high temperatures. The increase in the torsion number represents an improvement in the hot-working characteristics.

The hot-workability of the alloy depends on the ductility of grain boundaries, ductility of the matrix, non-metallic inclusions, precipitates and so on. For improvement of the matrix ductility, a content of from 35% to 65% of Ni and of from 15% to 35% of Cr are most desirable, and for improvement of the ductility of grain boundaries, it is necessary to decrease the segregations and precipitates at the grain boundaries. Mn, Cu and Si segregate at grain boundaries and deteriorate the workability of the alloy. The grain boundary segregation of these elements is smallest when nickel is present in the range of from 35% to 65% and chromium is present in the range of from 10% to 25%. When the nickel content is less than 35% segregation of copper becomes large, while when the nickel content is more than 65% segregation of manganese and silicon becomes large. Thus, 35 to 65% of Ni and 10 to 25% of Cr assure the smallest segregation in the case of ordinary solidification, and an alloy having these Ni and Cr content ranges has a strong corrosion resistance in a neutral, oxidizing or reducing gas atmosphere, such as Ar, He, CO and H_2, when containing a small amount of impurities.

Detailed explanations will now be made on the reasons for defining the ranges of each of the elements comprised in the heat-resistant alloys of the invention.

Carbon is effective to improve tensile strength, heat-resistant properties such as creep strength and creep rupture strength, which are required for a heat-resistant alloy, and at least 0.01% of carbon is required for these purposes. These properties can still be obtained when carbon is present together with carbide-forming elements such as Mo, Ti and V if the carbides are present in a finely distributed state. However, an excessive carbon content forms too large carbides which are detrimental to these properties. Thus, the upper limit of the carbon content is defined at 0.5%, and it is preferred that the carbon content is in the range of from 0.08% to 0.40%.

Silicon, when contained in an austenite alloy, remarkably reduces scaling at high temperatures and improves tensile strength. These effects are obtained when silicon is present in an amount of 0.01% or more, but an excessive silicon content precipitates the ferrite, and the austenite becomes unstable, lowering the heat resistance properties and the hot-working characteristics. A preferable range of the silicon content extends to not more than 0.15%, but up to 2.0% of silicon is allowed to be present for obtaining the required strength. According to certain Examples of the alloy of the invention, the silicon content lies in the range of from 0.3% to 0.50%.

When manganese is contained in an amount of 0.01% or more, it stabilizes the austenite and forms carbides which improve creep strength. Up to 3.0% of manganese may be contained for the above purpose. An excessive manganese content lowers the solubility of copper into the austenite and segregates Cu-enriched phases of low melting point at the grain boundaries of the austenite, thus remarkably deteriorating the hot-working characteristics and heat resistant properties. For this reason, a smaller amount of manganese is more desirable, and a preferable range is 0.01 to 0.15%. However, certain Examples of the alloy of the invention utilise a range of manganese from 0.20% to 1.50%.

It is well known that nickel and chromium are indispensable for improving heat-resistant properties at high temperatures and producing the austenite matrix. For example, many heat-resistant alloys have been developed from an austenitic 15/15 Ni/Cr heat-resistant steel. However, these known alloys have not been developed sufficiently so as to withstand severe hot-working.

The contents of nickel and chromium in the present invention are defined so as to maintain heat-resistant properties as required for a heat-resistant alloy and to obtain excellent hot-working characteristics. Namely, 22% to 80% of Ni and 10% to 40% of Cr form a stabilized austenite to give excellent hot-workabilities, and a preferred range of these elements is 23% to 75% and 15% to 33.3% respectively.

In an austenite-forming range outside the above ranges the improvement of the hot-working characteristics is small as compared with that obtained in the present inventive ranges, or the remarkable effects on the other heat-resistant properties are not produced although some improvement of hot-working characteristics may be obtained.

Ranges of from 35% to 65% of Ni and 10% to 25% of Cr are preferred for preventing the intergranular segregation of Mn, Cu, Si and other constituents.

Heat-resistant properties, and particularly the hot-working characteristics of the austenite produced by the above composition are already most excellent, but one or both of B and Zr and one or more of Ce, Mg and Be and also optionally Y are contained in the present inventive alloys for giving hot-working characteristics enough to withstand severe production conditions.

When B is present in an amount of 0.0005% or more in an austenitic heat-resistant alloy, the creep strength is improved, as well as the hot-working characteristics at high temperatures, particularly in a temperature range of 1,100° to 1,150°C. If the content of B is greater than 0.2%, borides are formed and the beneficial effect of the B is lowered. Thus the content of B is defined as 0.0005% to 0.2%, and preferably 0.003% to 0.05%.

When Zr is contained in an amount of 0.001% or more, the heat-resistant properties are improved as is the case with the addition of B. When Zr is present at the grain boundaries, it reacts with carbon to form MC carbides which improve intergranular ductility and improve hot-working characteristics below 1,100°C. An excessive content of Zr forms too large carbides which tend to offset the desirable effect of the addition of Zr, thus the upper limit of Zr is set at 6.0%. On the high-carbon side of the present invention, when the Zr content is more than eight times of the carbon content, the alloy shows a tendency to embrittlement. Thus a preferable range of the Zr content is 0.01 to 1.0%, and a particularly preferred range is 0.04% to 0.80%.

Ce, Mg and Be prevent the principal elements such as Fe, Ni and Mn from being sulphurated or oxidized during the steel making process and thus being partially wasted as impurities, and they are effective to clean the steel and decompose the sulphides remaining at the boundaries of solidifying grains and to divide them into fine spheres, thus improving the hot-working characteristics above 1,100°C. These effects can be obtained when any of these elements is present in an amount of 0.001% or more, but an excessive content of these elements reduces their above effects. Thus, the upper limit of these elements are defined as 0.5% for Ce, 0.2% for Mg, and 1.0% for Be. Only one of these elements may be added, or more than one may be added if desired. Preferred ranges of these elements are 0.02 to 0.50% for Ce, 0.03% to 0.10% for Mg, and 0.02% to 0.50% for Be.

In addition to the above, Y may be added, with the proviso that the alloy always contains one or both of Y and Ce. Y is effective by producing nitrides, carbides or intermetallic compounds and thus improves the heat-resistant properties and the corrosion resistance. Y, when present, should be contained in an amount of at least 0.05%, but in order to avoid the formation of too large nitrides, carbides or intermetallic compounds, its content should not exceed 10.0%.

Furthermore one or more of Mo, W, Co, Ti, Nb, Ta, Al, V and Cu may be added selectively to the alloy of the present invention. These elements form carbides, nitrides, or intermetallic compounds and improve the heat-resistant properties. Cu is also effective to give the alloy corrosion resistance. The effects of these elements are observed when Mo, W and Co are present in an amount of 0.1% or more, and when Ti, Nb, Ta, Al, V and Cu are present in an amount of 0.05% or more each (also 0.05% in total). An excessive amount of these elements forms too large carbides, nitrides or intermetallic compounds and this lowers the hot-working characteristics. Thus, the upper limits of these elements are defined as 10% for Mo and W, 30.0% for Co, 10% for Ti, Al, Nb, Ta, V and Cu when used alone, or when two or more of the latter six are used in combination.

Regarding Cu, this causes segregation at grain boundaries together with Mn and Si and deteriorates the hot-working characteristics. Thus it is desirable to restrict the copper content to be as small as possible, and its preferred range is 0.05 to 0.1%.

Preferred alloys of this invention have Co, Mo and Nb contents of, respectively, 0.5 to 10%, 0.5 to 1.0% and 0.1 to 0.15%.

Further, other elements such as P and S which are contained as unavoidable impurities should be maintained as low as possible because these damage the heat resistant properties. A particularly preferred alloy composition of this invention consists of, by weight, C in the range of from 0.01% to 0.45%, Si in the range of from 0.01% to 0.15%, Mn in the range of from 0.01% to 0.15%, Ni in the range of from 35% to 65%, and Cr in the range of from 10% to 25% as basic constituents, together with one or more of Mo in the range of from 0.1% to 10%, Co in the range of from 0.1% to 10%, W in the range of from 0.1% to 10%, B in the range of from 0.001% to 0.03%, Zr in the range of from 0.01% to 1.0%, Ce in the range of from 0.01% to 0.1%, Mg in the range of from 0.001% to 0.01%, Be in the range of from 0.001% to 0.1%, Ti in the range of from 0.2% to 4.5%, Al in the range

of from 0.2% to 4.5%, Y in the range of from 0.05% to 0.1% and Cu in the range of from 0.05% to 0.1%, and also comprising one or more of Nb, V and Ta each in the range of from 0.1% to 4.5%, the remainder being Fe and unavoidable impurities, the alloy containing at least some Fe.

The heat-resistant alloy of the present invention can be produced by an ordinary production method which includes melting and refining in a converter or electric furnace, ingot-making and breaking-down, or continuous casting into slabs and hot rolling into wires or plates for commercial use. When the alloy of the present invention is produced by electro-slag refining, still further improved hot-working characteristics are obtained. The hot rolled wires and plates may be subjected to temper treatments or cold rolling in combination with temper treatments for final use.

An advantage of the alloy having a chemical composition according to the invention is that it tends not to crack under severe hot-working conditions, and has an improved torsion number.

By way of example, certain specific alloys of the invention will now be described with reference to the following Table.

The Table shows the chemical compositions of 15mm thick plates produced by melting in an electric furnace, ingot-making, breaking-down and hot rolling, and the heat-resistant properties including the hot torsion numbers to show the hot-working characteristics at 1,100°C, and the creep rupture strength.

In the Table, the alloys A, C and G fall outside the scope of this invention, and are included for comparison with the alloys of the invention.

It is clear from the table that all of the alloys of the invention show remarkably improved heat-resistant properties as compared with the known comparative alloys.

The accompanying drawing is a graph showing the synergistic effect of Zr and Ce on the torsion number of an alloy of the invention, related to the hot-working temperature.

TABLE

Designation of Alloy	Kind of Alloy	Chemical Compositions (%)							
		C	Si	Mn	Ni	Cr	Fe	B, Zr	Ce, Mg, Be
A	Comparative	0.40	0.95	1.50	20.0	25.0	Balance	B: 0.003 Zr: 0.07	
B	Inventive	0.40	0.95	1.50	23.0	25.0	,, 57,54	B: 0.008	Be: 0.30 Ce: 0.40
C	Comparative	0.08	0.30	0.20	75.0	15.0	,,		Mg: 0.01 Ce: 0.02
D	Inventive	0.08	0.30	0.20	75.0	15.0	,, 7,67	B: 0.01	Mg: 0.05 Be: 0.07
E	,,	0.08	0.30	0.20	75.0	15.0	,,	Zr: 0.07	Be: 0.15
F	,,	0.08	0.30	0.20	75.0	15.0	,,	Zr: 0.15 B: 0.015	Ce: 0.1
G	Comparative	0.08	0.50	0.80	55.0	33.3	,,	Zr: 0.07	
H	Inventive	0.08	0.50	0.80	55.0	33.3	,,	Zr: 0.07 B: 0.003	Ce: 0.02

TABLE (Continued)

Designation of Alloy	Kind of Alloy	Chemical Composition (%) Mo, W, Co, Ti, Nb, Ta, Al, V, Cu, Y	Heat Resistant Properties: Hot Torsion Numbers at 1000°C	Heat Resistant Properties: Creep Rupture Strength at 1000°C for 10^3 hrs. Kg/mm²
A	Comparative	Co: 0.5	10.0	1.5
B	Inventive	Co: 0.5	19.5	1.8
C	Comparative	Co: 0.5, Mo: 1.0, Y: 0.02, Nb: 0.1	8.0	1.0
D	Inventive	Co: 0.5, Mo: 1.0, Y: *, Nb: 0.1	18.0	1.4
E	,,	Co: 0.5, Mo: 1.0, Y: *, Nb: 0.1	22.0	1.2
F	,,	Co: 0.5, Mo: 1.0, Y: *, Nb: 0.1	24.0	1.5
G	Comparative	Mo: 0.5, Al: 0.4, Ti: 0.4	3.5	2.8
H	Inventive	Mo: 0.5, Ti: †, Nb: 0.15	13.3	3.0

* The Y content lies in the range of from 0.05 to 10%.

† The Ti content lies in the range of from 0.05 to 10%

WHAT WE CLAIM IS:—

1. A heat-resistant alloy consisting of (by weight):

from 0.01 to 0.5% of C,
from 0.01 to 2.0% of Si,
from 0.01 to 3.0% of Mn,
from 22 to 80% of Ni, and
from 10 to 40% of Cr

as basic constituents; together with one or both of:

from 0.0005 to 0.20% of B, and
from 0.001 to 6.0% of Zr;

and one or more of:

from 0.001 to 0.50% of Ce,
from 0.001 to 0.2% of Mg,
from 0.001 to 1.0% of Be;

the alloy optionally containing from 0.05 to 10% of Y, with the remainder being Fe and unavoidable impurities, the alloy always containing one or both of Y and Ce, and at least some Fe.

2. The modification of the heat-resistant alloy as claimed in claim 1, which modified alloy additionally comprises (by weight) one or more of:

from 0.1 to 10.0% of Mo,
from 0.1 to 10.0% of W, and
from 0.1 to 30% of Co,

and, as further constituents, one or more of Ti, Nb, Ta, Al, V, Cu, each, when present, being in the range of from 0.05 to 10%, which further constituents and Y if present together comprise between 0.05 and 10% of the total weight of the alloy.

3. An alloy as claimed in any of the preceding claims, wherein the C content is in the range of from 0.08% to 0.40%, by weight.

4. An alloy as claimed in any of the preceding claims, wherein the Si content is in the range of from 0.30% to 0.50%, by weight.

5. An alloy as claimed in any of the preceding claims, wherein the Mn content is in the range of from 0.20% to 1.50%, by weight.

6. An alloy as claimed in any of the preceding claims, wherein the Ni content is in the range of from 23% to 75%, by weight.

7. An alloy as claimed in any of the preceding claims, wherein the Cr content is in the range of from 15.0% to 33.3%, by weight.

8. An alloy as claimed in any of the preceding claims, wherein the B content, when present, is in the range of from 0.003% to 0.05%, by weight.

9. An alloy as claimed in any of the preceding claims, wherein the Zr content, when present, is in the range of from 0.04% to 0.80%, by weight.

10. An alloy as claimed in any of the preceding claims, wherein the Ce content, when present, is in the range of from 0.02% to 0.50%, by weight.

11. An alloy as claimed in any of the preceding claims, wherein the Mg content, when present, is in the range of from 0.03% to 0.10%, by weight.

12. An alloy as claimed in any of the preceding claims, wherein the Be content, when present, is in the range of from 0.02% to 0.50%, by weight.

13. An alloy as claimed in any of the preceding claims, wherein the Co content, when present, is in the range of from 0.5% to 10.0%, by weight.

14. An alloy as claimed in any of the preceding claims, wherein the Mo content, when present, is in the range of from 0.5% to 1.0%, by weight.

15. An alloy as claimed in any of the preceding claims, wherein the Nb content, when present, is in the range of from 0.1% to 0.15%, by weight.

16. A heat-resistant alloy as claimed in claim 2, which alloy consists of, by weight, C in the range of from 0.01% to 0.45%, Si in the range of from 0.01% to 0.15%, Mn in the range of from 0.01% to 0.15%, Ni in the range of from 35% to 65%, and Cr in the range of from 10% to 25% as basic constituents, together with one or more of Mo in the range of from 0.1% to 10%, Co in the range of from 0.1% to 10%, W in the range of from 0.1% to 10%, B in the range of from 0.001% to 0.03%, Zr in the range of from 0.01% to 1.0%, Ce in the range of from 0.01% to 0.1%, Mg in the range of from 0.001% to 0.01%, Be in the range of from 0.001% to 0.1%, Ti in the range of from 0.2% to 4.5%, Al in the range of from 0.2% to 4.5%, Y in the range of from 0.05% to 0.1%, and Cu in the range of from 0.05% to 0.1%, and also comprising one or more of Nb, V and Ta each in the range of from 0.1% to 4.5%, the remainder being Fe and unavoidable impurities, the alloy containing at least some Fe.

17. A heat-resistant alloy as claimed in claim 1, or in claim 2 or in claim 16 and substantially as hereinbefore described especially with reference to the Examples.

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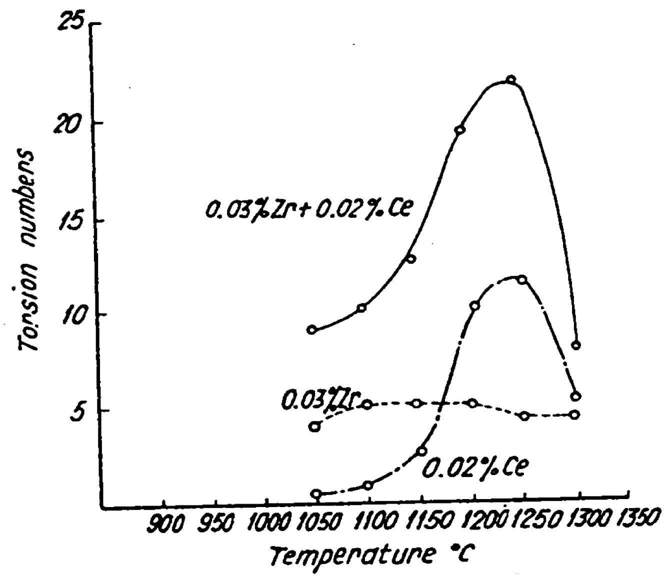
25
20
15
10
5
Torsion numbers
0.03%Zr+0.02%Ce
0.03%Zr
0.02%Ce
900 950 1000 1050 1100 1150 1200 1250 1300 1350
Temperature °C